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Investigating the potential for energy, fuel, materials and chemicals production from corn residues (cobs and stalks) by non-catalytic and catalytic pyrolysis in two reactor configurations

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Abstract

The results of thermogravimetric analysis (TGA), non-catalytic and catalytic pyrolysis of corn cobs and corn stalks are reported in this paper. Pyrolysis took place in two different reactor configurations for both feedstocks: (1) fast pyrolysis in a captive sample reactor; and (2) non-catalytic slow pyrolysis and catalytic pyrolysis in a fixed-bed reactor. Experiments were carried out in atmospheric pressure at three temperatures: low temperature (360–380 °C), medium temperature (500–600 °C) and at high temperature (600–700 °C). The results of the experimental study were compared with data reported in the literature. Investigating the potential of corn residues for energy, fuel, materials and chemicals production according to their thermochemical treatment products yields and quality, it can be stated that: (a) *corn stalks* could be suitable raw material for energy production via gasification at high temperature, due to their medium low heating value (LHV) of pyrolysis gas (13–15 MJ/m^3); (b) *corn cob* could be a good solid biofuel, due to the high LHV (24–26 MJ/kg) of the produced char; (c) additionally, corn cobs could be a good material for activated carbon production after being activated or gasified with steam, due to its high fixed carbon content(~74 wt%); (d) liquid was the major pyrolysis product from *catalytic pyrolysis* (about 40–44 wt% on biomass) for both feedstocks; further analysis of the organic phase of the liquid products were hydrocarbons and phenols, which make them interesting for chemicals production.

Keywords: Pyrolysis; Catalytic pyrolysis; Captive sample reactor; Fixed-bed reactor; Corn cob; Corn stalks

Contents

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1. Introduction

Biomass has been widely recognized as a clean and renewable energy source with increasing potential to replace conventional fossil fuels in the energy market. It is in abundance and stands as the third energy resource after oil and coal [1,2]. Using energy crops and agricultural residues for energy production it can be an alternative solution in the problem of waste disposal [3]. A significant advantage is that it can be converted to liquid, solid and gaseous fuels [1] and thus can contribute to the struggle against climate changes by replacing conventional fossil fuels [2,4].

During pyrolysis, biomass is heated in the absence of oxygen, or in a limited oxygen supply [5]. The pyrolysis process includes a very complex set of primary and secondary reactions involving the formation of free radicals [1]. Pyrolysis is classified into three types namely flash, fast and slow depending on the temperature, heating rate and residence time. Flash pyrolysis is a rapid heating rate process occurring at 400–900 °C with small residence time. Fast pyrolysis is differentiated from flash as the heating rates are not extremely high and the temperature is lower than 600 °C. Slow pyrolysis occurs at 450–700 °C with even lower heating rates. The main pyrolysis products are char, oil and gas. Char can be used for combustion or as activated carbon and the gaseous product can be used for energy production. The liquid product of biomass pyrolysis, known as bio-oil or pyrolysis oil, is a complex mixture of several hundreds of organic compounds that exhibit a wide range of chemical functionalities. Bio-oil consists of two phases, an aqueous phase containing oxygenated organic compounds of lower molecular weight and a non-aqueous phase, which contains organic compounds (mainly aromatics) and it is a very interesting pyrolysis product since it can be used either directly as a fuel or as a source of high value chemicals.

Corn is a significant crop all around the world. The annual production worldwide is about 520×10^9 kg. The major production regions are North America (42%), Asia (26%), Europe (12%) and South America (9%) [6]. According to FAO [7] worldwide production of corn in 2002 was 604×10^6 t cultivated in 1383×10^6 m^2, 134 of which were cultivated in Europe. Most corn though (about 64% of global production) is used for animal food. For human needs the percentage is 19%, while only 5% of global production is lost as waste. Wasted corn can be utilized as feedstock for bioethanol production [6]. The past 15 years, maize is used as raw material for bioethanol production, which has tripled up to 28×10^6 t in 2003. Corn residues may contain valuable materials and the current economic values are less than the apparent cost of collection, transportation and processing for beneficial use [8]. Recently this agricultural waste is being studied as a raw material for energy and active carbon preparation.

Several recent studies concerned the effect of various parameters in the pyrolysis products. Cao et al. [9] studied the behaviour of corn cob pyrolysis, where Sun et al. [10] studied the pyrolysis of corn stalk, both in a tube-type reactor. Putun et al. [11] studied also pyrolysis in a fixed-bed reactor focusing on the liquid and solid products. Lanzetta and Di Blasi [12] also studied the pyrolysis of corn straw focusing on the kinetics of the reactions. Rapid pyrolysis in a free-fall reactor has performed by Zanzi et al. [13], Encinar et al. [14] and Wei [15] using different kind of biomass. In their studies it was observed that hydrogen content was favored by a higher temperature and cellulose and hemi-cellulose content. The research of Tsai et al. [4] and Lee et al. [16] concerned fast pyrolysis conditions, where Lee et al. [16] focused on the prediction of gaseous products from biomass pyrolysis.

Since corn is the one of the most widely planted crops in the world and also in Greece, the purpose of the present work is to carry out research in order to study its behaviour through pyrolysis since literature data about liquid and especially gases products during pyrolysis are limited. In order to maximize the production of the derived products (gas, liquid and solid), as well as useful components in the gaseous and liquid fraction, the optimum reactor conditions were investigated. Two different reactor configurations were used and the effect of factors such as temperature and the presence of catalyst were studied. The ultimate purpose was the investigation of the potential of corn residues for energy, fuel, materials and chemicals production according to the obtained products yields and quality in laboratory scale.

2. Experimental

2.1. Biomass characteristics

The biomass used is corn cob and corn stalk collected from Orestiada, region of Thrace in the North-East Greece near the Greek-Turkish borders. After dust washing, corn leaf and corn

seed removal, the sample was grounded to desirable particle size and sieved to powder of <1 mm diameter. The elemental analysis of the samples was performed with the method ASTM-D 5291, based on combustion in an oven, by employing an elemental analyst CHN-LECO 800.

The proximate analysis was performed by thermogravimetric analysis (TGA). This method is used to determine a material's thermal stability and its fraction of volatile components by monitoring the weight change that occurs while a specimen is heated. All experiments with TGA comprised three main different steps: drying, devolatilization in inert atmosphere and combustion in oxygen [17].

The instrument used in this study was a type of TA Instruments 2960 in which the sample was heated with air according to the following temperature profile: the heating started at 30 °C with rate of 10 °C min^{-1} and stabilization at 100 °C for 20 min. Then, with a rate of 20 °C min^{-1}, the temperature increased up to 600 °C and remained constant for 20 min. With a rate of 20 °C min^{-1} the final temperature at 900 °C was achieved. The first weight loss is due to moisture evaporation, which takes place up to 150 °C. In the second step lighter volatiles are being burnt between 170 and 370 °C. This step was due to hemicellulose and cellulose decomposition. The third step occurs between 400 and 700 °C, where lignin decomposition takes place, heavier volatiles are burned. Up to 700 °C semi-coke is burned. Above 800 °C the remaining semi coke reacts with carbon dioxide [18,19]. What remained at the end of the char oxidation (900 °C) was ash. The results from the proximate and elemental analysis and the heating value of the raw material are presented in Table 1.

The determination of the heating value of the feedstock was performed by the ASTM-D 4809 method. A PAAR calorimeter was used, in which the combustion of each sample was taken place with pure oxygen. The moisture of corn cob and stalk was also determined by heating them at 105 °C in an oven for 3 h. Heating values and moisture content are also present in Table 1.

2.2. Fast pyrolysis in the laboratory captive sample reactor

The experimental apparatus for fast pyrolysis is made by a wire mesh sample reactor comprised of two electrodes, an electrical circuit, a water cooling coil, a trap for moisture, two filters for liquid hydrocarbons, a system for gas collection and a system of gas analyses (GC). The sample was weighted approximately 0.3 g and placed in an envelope of stainless steel 100 mesh. A thermocouple inside the sample, connected with a computer through program, provided the relation between temperature and time (heating rate). The experiments were carried out at 360, 520, 630 and 730 °C for cob and 380, 520, 630 and 680 °C for stalk, with a heating rate 52 °C/s for corn cob and 45 °C/s for corn stalk at atmospheric pressure in He. The reaction products included char, gas and volatile compounds. The solid product remained in the screen and was determined gravimetrically. The liquid product was comprised by tar and liquid hydrocarbons condensed within the reactor vessel, on the wall and flanges of the reactor and on the paper filter at the exit of the reactor. Hydrocarbons, in the vapor phase at room temperature were collected in two lipophilic traps containing 80:100 mesh Porapaq Q chromatographic packing, placed at the exit of the reactor and then measured gravimetrically. The produced gas is being collected in the water container. The volume of water displaced determined the gas volume. Fig. 1 shows the experimental

Table 1
Characteristics of agricultural residues (literature data and results from present study)

	Corncob Present study	Corn stalk Present study	Maize Encinar et al. [14]	Corn stalk Shuangning et al. [30]	Straw Zanzi et al. [13]	Legume straw Wei et al. [15]
Elemental analysis						
C	43.77	43.8	46.9	43.65	45.6	43.3
H	6.23	6.42	5.4	5.56	6.5	5.62
O	50	49.78	47.4	43.31	47	50.35
N			0.2	0.61	0.5	0.61
S			0.06	0.01		0.12
Proximate analysis (wt%)						
	TGA results					
Moisture	7.57	6.44			7.1	9.8
Light vol.	57.27	83.07	82.3	75.17		73.74
Heavy vol.	27.1	8.19				
Fixed carbon			14.8	19.25		14.84
Ash	8.06	2.3	2.9	5.58	3.2 (mf)	1.62
LHV (MJ kg^{-1})	18.25	18.17	15.4	17.19	17.08	

	Corn cob Garrote [31]	Corn stalk Banchorndhevakul [32]
Chemical analysis		
Cellulose (wt%)	34.3	32.4
Hemicelluloses (wt%)	40.53	40.8
Lignin (wt%)	18.8	2.5

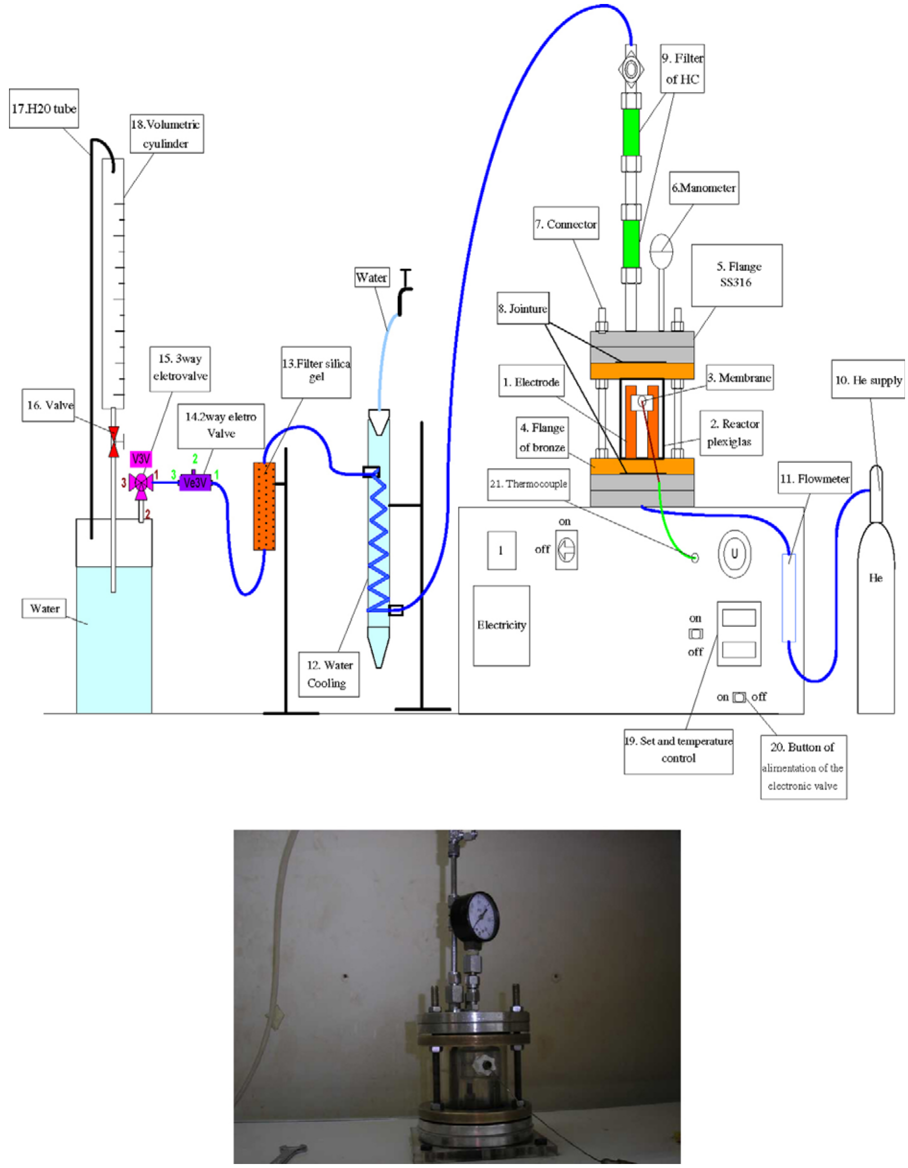


Fig. 1. Experimental set up of the captive sample reactor.

set up. An outline of both reactor and the whole procedure is also shown in another study [3].

The produced gas was analyzed in a gas chromatograph (6890N, Agilent Technology). The columns used were Plot Q and Molesieve, the carrier gas was helium and the injection volume was 1 μl. The temperature profile of the gas chromatograph was isothermal at 50 °C and the retention time of the whole analysis was 30 min. The standard gas mixture used for the calibration of the method was CO, CO_2, H_2, CH_4, C_2H_4 and C_2H_6, which all had concentration 1% (v/v) balanced in Helium. The volume concentration was calculated by an external standard method. Gas composition and yields were resulted based on a linear relationship between the concentration and area measured by the program. The produced gas composed mostly by CO, CO_2, H_2, CH_4, C_2H_4 and C_2H_6. The thermal conductivity detector (TCD) was used for the analysis of CO, CO_2, H_2, CH_4, C_2H_4 and C_2H_6 and the flame ion detector (FID) for CH_4, C_2H_4 and C_2H_6.

2.3. Slow pyrolysis in the laboratory fixed-bed reactor

A fixed-bed reactor (12.1 cm height and 1.25 cm i.d.) was used for the biomass non-catalytic pyrolysis experiments. It is a laboratory scale reactor, made of stainless steel 316 and heated by a three-zone furnace. The corn feedstock was introduced into the reactor through a piston system. A constant stream of N_2 was used in all steps of the pyrolysis experiments in order to achieve an inert atmosphere during pyrolysis and also for the removal of the pyrolysis products. In all experiments, the reactor was filled with 0.7 g of glassbeads (in the non-catalytic runs) or catalyst and the piston with 1.5 g biomass. As soon as the reactor reached the desired reaction temperature (500 °C) the biomass entered the reactor under a constant flow of N_2

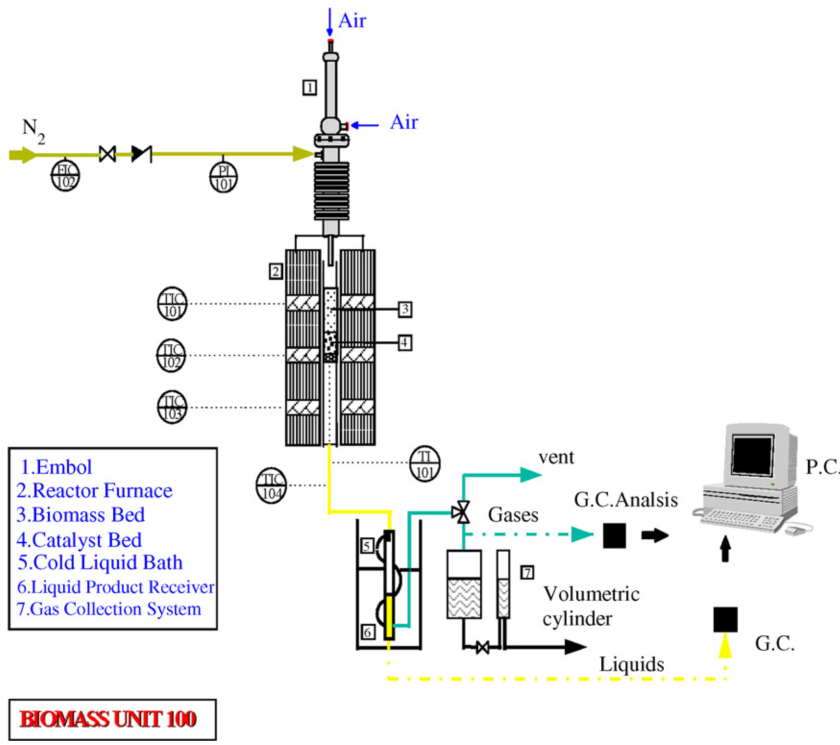


Fig. 2. Experimental set up of the fixed-bed reactor unit.

(100 cc/min for 15 min) and came in contact with the preheated catalyst or glass beads in the case of non-catalytic runs. The liquid products (bio-oil) were collected in a liquid bath (−17 °C) and quantitatively measured in a pre-weighted glass receiver. The two phases usually present in bio-oil (organic and aqueous) were separated with the aid of an organic solvent (dichloromethane). The gaseous products were collected and measured by water displacement and the amount of the solid residue (named as char) was measured by direct weighting. The solid residue left in the reactor after the end of each experimental run could include solid products such as charcoal, reacted products on the catalyst (char) as well as un-reacted biomass feedstock.

Gas chromatography and GC–MS were used for the analysis of the liquid and gaseous products, respectively. Gaseous products were analyzed in a HP 6890 GC, equipped with four columns (Precolumn: OV-101; Columns: Porapak N, Molecular Sieve 5A and Rt-Qplot (30 m × 0.53 mm i.d.)) and two detectors (TCD and FID). Liquid products were analyzed by GC–MS analysis in a HP 5989 MS ENGINE (electron energy 70 eV; Emission 300 V; Helium flow rate: 0.7 cc/min; Column: HP-5MS (30 m × 0.25 mm i.d. × 0.25 μm)) and internal libraries were used for the identification of the compounds found in the bio-oil and their categorization into main functional groups. A more detailed description of the experimental set up and the experimental unit are presented elsewhere [5]. Fig. 2 shows the experimental set up.

2.4. Catalytic pyrolysis in the laboratory fixed-bed reactor

The catalytic pyrolysis experiments were performed in the fixed-bed reactor described above using a catalyst instead of glass beads. The catalyst was received from a commercial FCC unit, provided by GRACE GmbH and Co. It is as called an 'equilibrium' catalyst. Properties and characteristics of this catalyst have been mentioned elsewhere [20].

3. Results and discussion

3.1. Elemental and thermogravimetric analysis of corn residues

The proximate and elemental analyses of both agricultural residues are shown in Table 1. It appears that both feedstocks fluctuate to the same values in terms of C, H, O and heating value (~43.8 wt%, 6.4%, 50% and 18.2 kJ kg^{-1}, respectively). The heating value (18 MJ/kg) is relatively high compared to other biomass feedstocks studied [3,14,30,13] which make those materials interesting for further study for energy production; There is a good correlation comparing these values with values from literature (Table 1).

The TGA curves (Fig. 3a and b) showed that the thermal decomposition of both corn cob and corn stalk included three steps. Moisture evaporation occurred up to 110 °C. Corn cob had higher amount (7.57 wt%) than stalks (6.44 wt%). The remaining solid (ash) was also higher in cob experiments (8.06 wt%).

The second step for corn cob occurred in the range of 210–390 °C, while for corn stalk in the range of 195–355 °C. The percent of light volatiles for the first sample was 57.27 wt% and for the second 83.07 wt%.

The third step for corn cob occurs between the temperature ranges 390 and 900 °C. For corn stalk the respective range is 355–900 °C. The weight loss there, representing the heavier

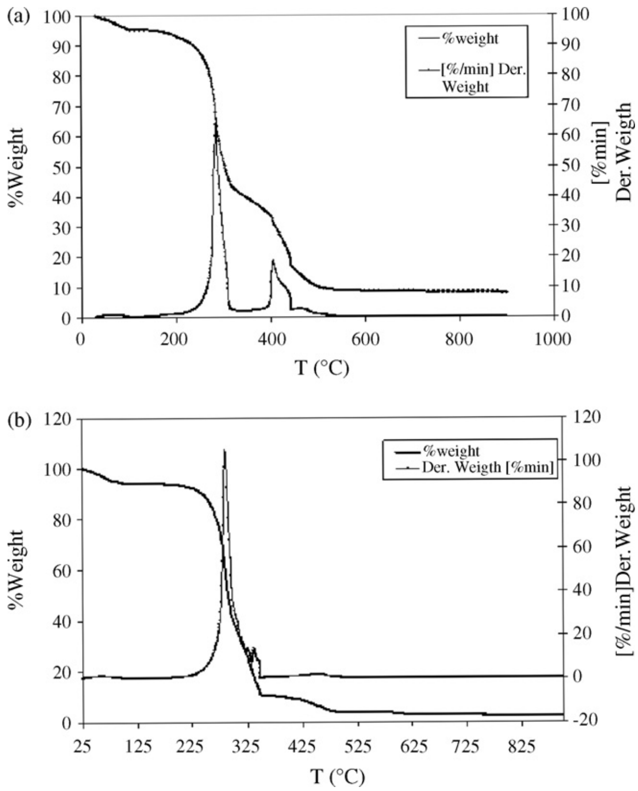


Fig. 3. (a and b) TGA of corn cob and stalk.

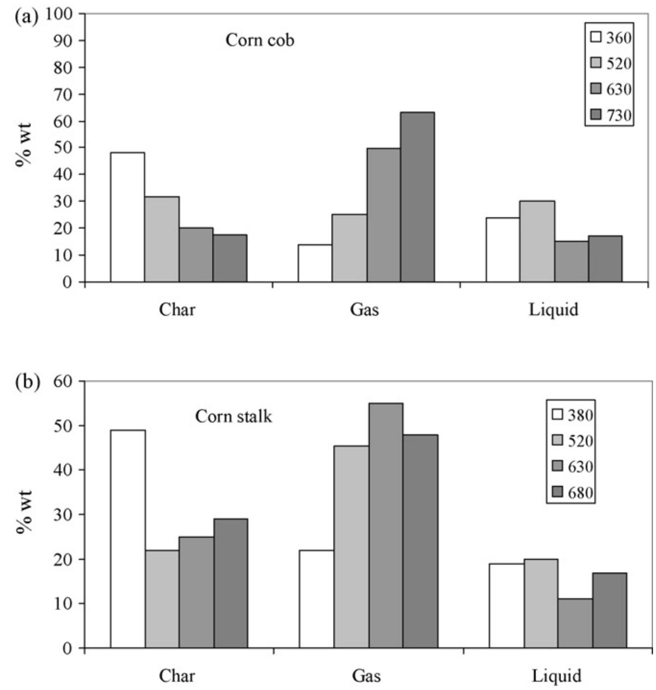


Fig. 4. (a and b) Effect of temperature on the yields of the products of corn cob and stalk pyrolysis in the captive sample reactor.

volatiles was for cob 27.1 wt% and 8.19 wt% for stalk. Both samples gave high amounts of volatiles (light and heavy), corn cob 84.37 wt% and corn stalk 91.26 wt%.

3.2. Experimental results of fast pyrolysis in the captive sample reactor

3.2.1. Product yields

Pyrolysis products are gaseous, liquid and solid. The yields of these products are determined by different factors, temperature being one of them. As mentioned above pyrolysis experiments in the captive sample reactor were carried out at 360, 520, 630 and 730 °C for cob, at a heating rate of 52 °C s^{-1}, and 380, 520, 630 and 680 °C for stalk, at a heating rate of 45 °C s^{-1}. As shown in Fig. 4a and b, and especially at Fig. 4a corn cob, by increasing the temperature of the reactor, volatiles are released from biomass particles, increasing the yield of the gaseous products and decreasing the char yield. The higher gas yield in this study was 63 wt% at 730 °C for corn cob and 55 wt% at 630 °C for corn stalk. The char yield for cob and stalk reached 48 wt% at 360 °C and 49 wt% at 380 °C, respectively. The higher yields of char are observed mostly at low temperatures, whereas the higher yields of gas are observed mostly at temperatures above 500 °C. Liquid comprised by hydrocarbons, tar and water. Liquid phase reached a maximum yield of 30 wt% for cob and 20 wt% for stalk at 520 °C. Fig. 5 shows the effect of temperature in the weight loss percent.

The above results are in good correlation with similar studies reported in the literature. Demirbas [21] studied the effect of temperature on the pyrolysis products of nut shells and reported a similar decrease in the char yield, an increase in the gaseous fractions and a maximum liquid yield at temperatures between 400 and 530 °C depending on the type of the nut feedstock. Cao et al. [9] studied the pyrolysis of corn cob in a tube-typed reactor and also found maximum char yield and lower gas yield at lower temperatures. The liquid yield in this study decreased with an increase in temperature between 350 and 600 °C.

3.2.2. Gas composition

The composition of the gaseous products was calculated by the chromatographic analysis. The produced gas is composed mostly of CO, CO_2, H_2, CH_4, C_2H_4 and C_2H_6. As mentioned above increasing the temperature, gas yield increase due to the secondary reactions of pyrolysis vapors. Under fast heating and pyrolysis conditions, dehydration and pyrolysis processes could happen simultaneously. This provides the opportunity for producing more hydrogen and carbon monoxide [14,15].

Fig. 6a and b show the effect of temperature on the gas composition. In higher temperatures the percentage of CO, H_2

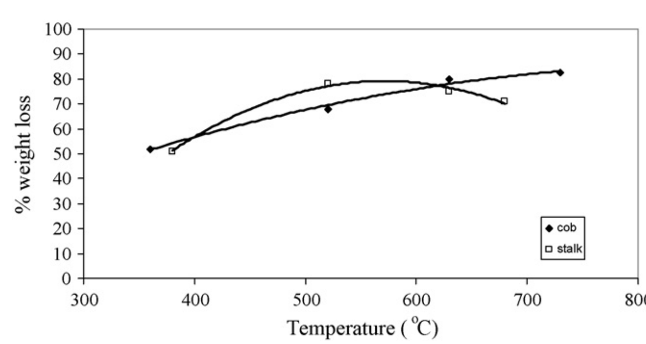
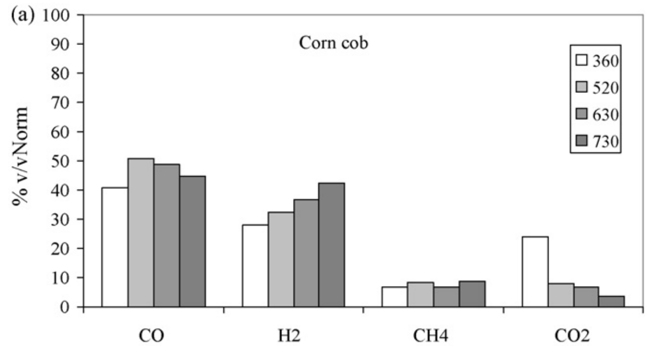


Fig. 5. Effect of temperature on the total weight loss for corn cob and stalk.



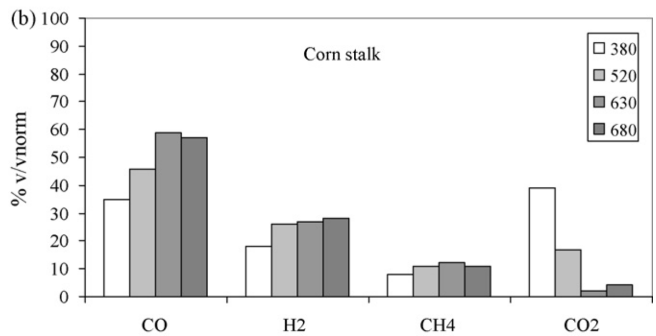


Fig. 6. (a and b) Effect of temperature on the concentration of CO, H_2, CH_4 and CO_2 produced from corn cob and corn stalk in the captive sample reactor.

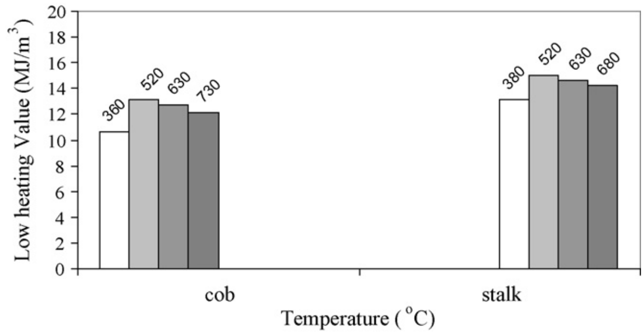


Fig. 7. Effect of temperature on the heating value of the produced gas from corn cob and stalk.

and CH_4 is increasing, and CO_2 is decreasing. Though, above 600 °C CO has a tendency to decrease. The highest amount in the gas composition was the one of carbon monoxide 51% (v/v) for cob and 59% (v/v) for stalk residues, followed by hydrogen 46.5% (v/v) for cob and 28% (v/v) for stalk. Carbon dioxide reached the higher values (24 and 39%, v/v for cob and stalk, respectively) at lower temperatures. Methane gave maximum values 9% (v/v) for cob and 12% (v/v) for stalk, and there were also traces of ethylene and ethane.

The high yields of syngas (H_2 and CO) might be due to the increased content of cellulose and hemicellulose in the raw material (Table 1). Biomass composed of higher cellulose and hemicellulose content produces a relatively higher hydrogen-rich gas yield than that composed of higher lignin. This can explain the higher amounts of H_2 and CO determined in the pyrolysis of corn cob, which is expected to contain more cellulosic than lignin polysaccharides. The increased carbon monoxide content could also be due to the gasification reaction:

$$C + CO_2 \rightarrow 2CO$$

The low heating value (LHV) of the gas was calculated by using Eq. (1), [22,23], the molar ratio of CO, H_2, CH_4 and hydrocarbons C_2H_4, C_2H_6.

$$LHV = (30.0 \times CO + 25.7 \times H_2 + 85.4 \times CH_4 + 151.3 \times C_nH_m)4.2, \quad KJ/m^3 \tag{1}$$

The LHV of gas products ranged between 10–13 MJ m^{-3} for corn cob, and 13–15 MJ m^{-3} for corn stalk, (Fig. 7), which according to Yang et al. [22] belongs to the medium level gas fuels and can be directly used in engines, turbines and boilers for power production.

3.2.3. Char quality

Concerning char analysis, char produced in higher temperatures has higher reactivity because of the increase of the ash content. If the temperature is high then the heating rate is increased. An increased heating rate favors the char reactivity.

In the present study the composition of fixed carbon in char increases up to a maximum value and then decreases again. For corn cob the maximum value is 73.71 wt% at 630 °C, where for corn stalk is 62.18 wt% at 520 °C. Results are shown in Table 2. The carbon content of the residue usually increases with temperature. However, a decrease is often observed between 600 and 700 °C, which can be attributed to the increased production of carbon containing compounds in the gaseous product.

The heating value of the char was calculated by Eq. (2) using the wt% of C, H and O from the elemental analysis of the char.

$$CV = 0.34 \times \%C + 1.4 \times \%H - 0.16 \times \%O, \ (MJ/kg) \tag{2}$$

Table 2
Elemental analysis and heating value of pyrolysis char in the captive sample reactor

Raw material	Pyrolysis temperature (°C)	Composition (wt%)			
		C	H	O	HV (MJ/kg)
Corn cob	520	67.62	4.14	28.24	24.27
Corn cob	630	73.71	3.12	23.17	25.72
Corn cob	730	69.26	3.45	27.29	24.01
Corn stalk	520	62.18	2.59	35.23	19.13
Corn stalk	630	60.54	2.64	36.82	18.39
Corn stalk	680	50.24	5.15	44.61	17.15

Table 3
Comparison of product yields from pyrolysis of both corn feedstocks at 500 °C for non-catalytic and catalytic pyrolysis

	Products			
	Non-catalytic pyrolysis		Catalytic pyrolysis	
	Corn stalks	Corn cob	Corn stalk	Corn cob
Gas	14.47	16.16	15.29	12.26
Char	32.67	37.31	30.62	32.99
Liquid	42.22	40.22	41.18	43.64
Aqueous liquid phase	*22.49*	*20.00*	*27.82*	*30.07*
Organic liquid phase	*17.78*	*18.05*	*11.35*	*1*
Mass balance	89.37	93.69	87.09	89.00

The results (Table 2) show that corn cob gave higher heating value than corn stalk. The higher value for both samples (24.27 and 19.13 MJ/kg for cob and stalk, respectively) was given for the higher percentage of carbon.

3.3. Experimental results of fixed-bed pyrolysis

3.3.1. Product yields

Non-catalytic runs have been performed with both corn cob and corn stalks. Results from corn pyrolysis experiments are presented in Table 3 and Fig. 8a and b. It would be useful to point that the results presented in the current study are averages of repeatable runs. All mass balances achieved were between 90% and 93%.

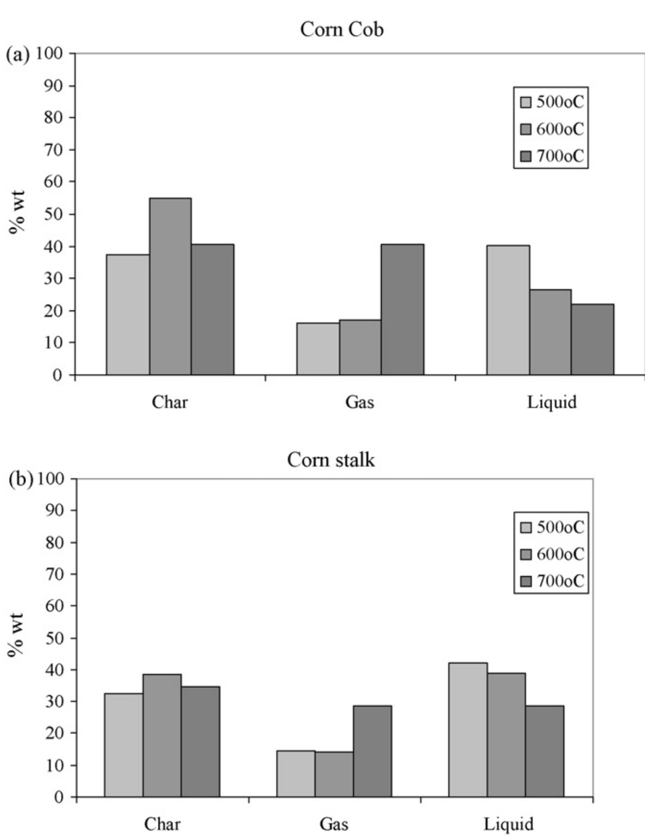


Fig. 8. (a and b) Effect of temperature on the yields of the products of corn cob and stalk pyrolysis in the fixed-bed reactor.

Table 3 shows the behaviour of both feed stocks is comparable in terms of the main pyrolysis products. This was expected and can be justified by the similar chemical and physical properties of the two feed stocks also presented in Table 1. The similarities also concern the organic part of the liquid product which was found to be close to 18 wt% (on biomass base) in both cases. However, the aqueous phase of the produced bio-oil is slightly higher in the case of corn stalk. The production of gas does not seem to alter significantly with the presence of different types of corn, exhibiting slightly higher values in the case of corn cob (up to 16%).

In order to estimate the effect of temperature in the product yields of the pyrolyzed corn cob and stalks, a series of non-catalytic experiments were carried out at 500, 600 and 700 °C. As shown in Fig. 8a and b in terms of products yields, the higher the temperature resulted in an increase in the yield of gases emitted and a decrease in the liquid product [21,24]. The liquid product reaches a minimum yield of approximately 29 wt% and 22 wt% on biomass at 700 °C for corn stalk and corn cob, respectively. Previous studies with other biomass feedstocks showed that temperatures close to 500 °C appear the maximum liquid yield [25–27]. Devolatilization reactions are favored by increased temperature and therefore gas yield is increased at approximately 29 wt% and 40 wt% on biomass at 700 °C for corn stalks and corn cob, respectively. The coke product does

Table 4
Comparison of gas composition (v/v, %) from the pyrolysis of the two corn feedstocks in the fixed-bed reactor at 500 °C

Gaseous products	Non-Catalytic pyrolysis		Catalytic pyrolysis	
	Corn stalks	Corn cob	Corn stalks	Corn cob
H_2	2.42	1.82	1.56	4.20
CO	34.77	38.21	35.02	37.01
CO_2	52.36	51.69	52.26	48.07
C_2=	0.83	1.28	0.92	0.88
C_2	1.02	0.69	1.16	0.90
CH_4	5.49	4.08	5.78	6.05
C_3=	0.58	0.67	0.85	0.80
C_3	0.25	0.12	0.31	0.17
nC_4	0.85	0.58	0.88	0.69
iC_5	0.95	0.69	0.88	0.79
nC_5	0.07	0.00	0.12	0.08
C_6(+)	0.41	0.17	0.27	0.37
Total	100.00	100.00	100.00	100.00

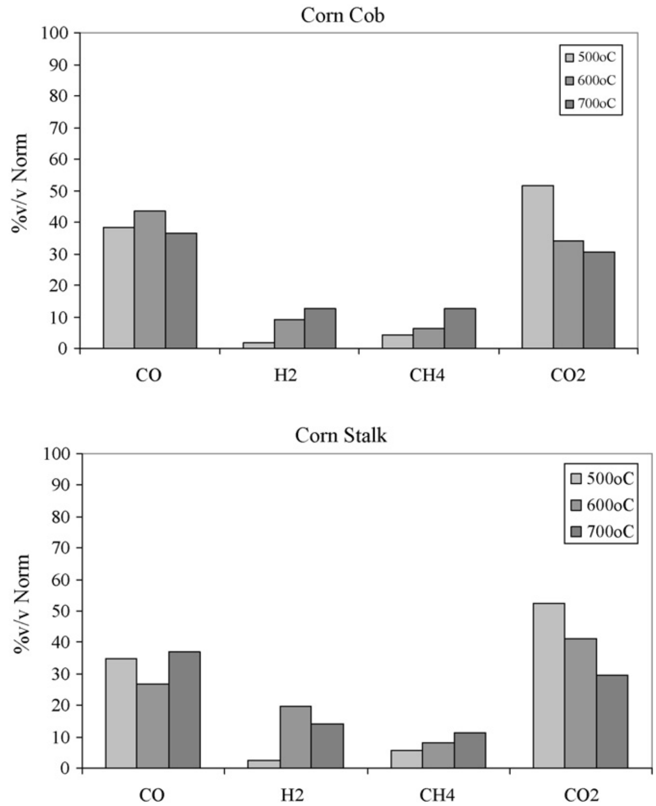


Fig. 9. (a and b) Effect of temperature on the concentration of CO, H_2, CH_4 and CO_2 produced from corn cob and corn stalk in the fixed-bed reactor.

not exhibit significant increasing or decreasing trend, but it seems to appear a maximum yield at 600 °C for both corn feed stocks.

3.3.2. Gas composition

The analysis of the produced gases from biomass pyrolysis non-catalytic tests is presented in Table 4 for both feeds tocks. The oxygen containing compounds (CO_2 and CO) are the dominant compounds (more than 80 vol% in most of the cases under study) and CH_4 is the hydrocarbon produced in the higher concentration (about 5%). The concentration of the hydrogen in these studies was not particularly high (about 1–2.5 vol%), at least as far as the non-catalytic runs are concerned. Attempting a comparison between the two feed stocks, one would not be able to identify any significant differences, apart from a slight decrease in the production of higher hydrocarbons (C_3–C_6) in the corn cob experiments.

The effect of temperature in the gas composition is shown in Fig. 9a and b. Gases identified during the pyrolysis of the two corn feeds tocks were H_2, CO_2, CO, CH_4 and low molecular weight hydrocarbons such as C_2–C_6. As it can be seen increase of temperature decreased the CO_2 production, increased the CH_4 production, whereas H_2 production appears a significant increase at 600 °C for the pyrolysis of corn stalk. CO production did not present any substantial change. For both feeds tocks the highest amount on the produced gas consists of CO_2 and CO (about 70 vol% on gas produced).

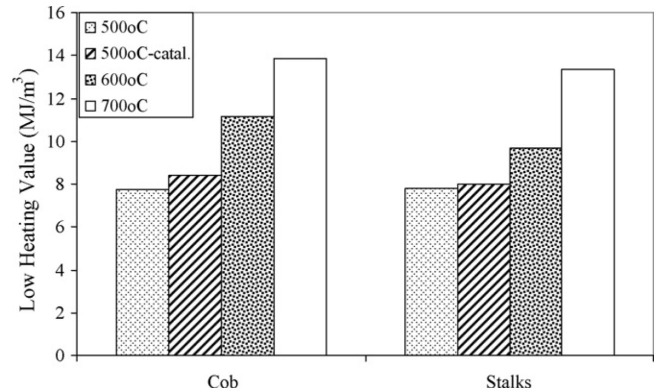


Fig. 10. Low heating value of gaseous products from catalytic and non-catalytic pyrolysis of corn cob and corn stalk in the fixed-bed reactor.

Low heating value was calculated for both samples using Eq. (1). The results (Fig. 10) are similar for the two feed stocks, differing only at 600 °C, where corn cob gave higher value.

Table 5 shows the pyrolysis results from both corn samples for both reactors. Literature data are also presented verifying that there is a relatively good correlation between them.

3.3.3. Bio-oil quality

Only the fraction of organic compounds soluble in dichloromethane, was further analyzed with GC–MS. This fraction should contain all the organic compounds in the bio-oil which are of medium or no polarity, such as phenols and hydrocarbons, and it was found to be between 17 wt% and 18 wt% on biomass (Table 3). The remaining aqueous phase should contain all the water produced from the pyrolysis process together with all the water-soluble organic compounds and was not analyzed any further in the current study. The main fractions from GC–MS analysis are presented in Fig. 11a and b.

Several hundreds organic compounds have been determined in the different types of the bio-oil produced, which cover a wide range of the organic chemistry and are responsible for a variety of the bio oil properties. An increased fraction of small molecular weight, oxygenated compounds would result to a reduction in the calorific value of the liquid produced. The presence of the carboxylic acids in the bio-oil is also an important factor for its quality of the liquid in terms of its corrosivity, and finally the presence of carbonyls is related to its stability. All the above are considered to be very important factors if the bio-oil produced is going to be used as a fuel. The yields of phenols and hydrocarbons, which are useful chemicals that can be obtained from bio-oil, are also expected to be increased in bio-oils of desirable quality.

As it can be seen from Fig. 11a and b, the pyrolysis of corn stalks seems to produce a more interesting bio-oil fraction, since it favors the production of hydrocarbons and phenols even in the absence of catalyst, which indicates the strong influence of the feedstock on the products of biomass pyrolysis. It is worth mentioning at this point, that, compared to conventional (non-catalytic) biomass pyrolysis experiments studied elsewhere in the presence of other feeds tocks [5,20], the amount of phenols produced is quite high. Concerning the production of

Table 5
Comparison of present study results with literature data

Residue type	Reference							
	Present study		Present study		Encinar et al. [14]	Cao et al. [9]	Zanzi et al. [13]	Wei et al. [15]
	Corn cob	Corn stalk	Corn cob	Corn stalk	Maize	Corn cob	Straw	Legume straw
Reactor type	Captive sample		Fixed-bed (non-catalytic)					
Operation temperature (°C)	360–730	380–680	500–700	500–700	400–700		800	500–800
Production yields								
Gases	14–63[a]	22–55[a]	16–40[a]	14–29[a]	28–40	27–41[a]	75.8[b]	32–70
Liquid	15–30[a]	11–20[a]	22–40[a]	29–42[a]	34–40	34–41[a]	0.9[b]	6–18
Char	17.6–48[a]	22–49[a]	37–55[a]	33–39[a]	26–36	24–32[a]	13.2[b]	9–21
Water and losses							10.1[b]	13–28
Gas composition								
CO	41–51[c]	35–59[c]	37–44[c]	27–37[c]	1.8–3[d]	28–40[e]	28[f]	35–43
CO_2	3.5–24[c]	2–39[c]	31–52[c]	30–52[c]	1.7–2.3[d]	52–71[e]	23.7[f]	7–35
H_2	28–42.5[c]	18–28[c]	2–13[c]	2–20[c]	0.07–9.8[d]	1–7[e]	35[f]	20–27
$H_2 + CO$						50[e]		
CH_4	7–9[c]	8–12[c]	4–13[c]	5–11[c]	0.04–1.2[d]	0–3[e]	9.5[f]	9–13
C_2H_6/C_2H_4	0–1[c]	0–1[c]	1–4[c]	1–4[c]		0–1[e]	0.1/3.1[f]	0–5
LHV of gas (MJ m^{-3})	10–13	13–15						

[a] (wt%).
[b] (wt%, Maf).
[c] (v/v, %) Norm.
[d] (mol kg^{-1}).
[e] (v/v, %).
[f] (mol% dry).

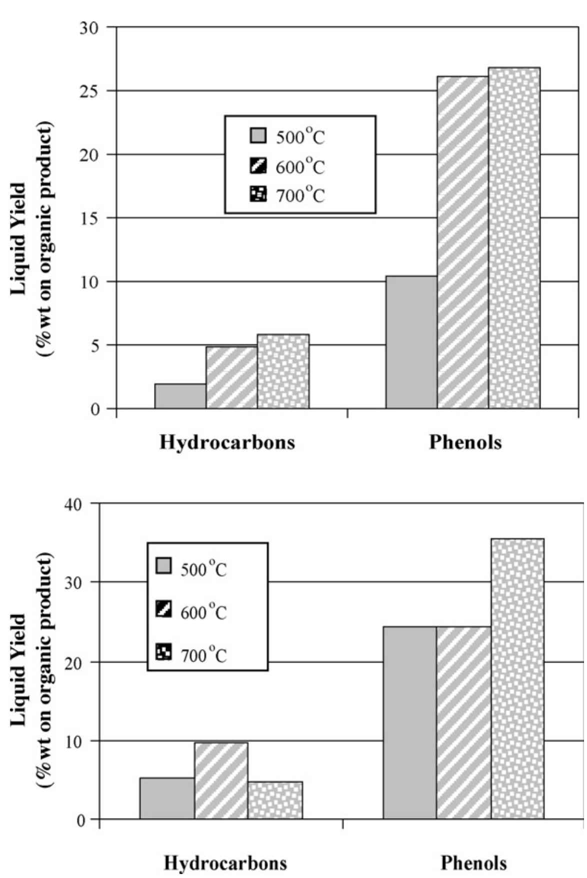


Fig. 11. (a and b) Effect of temperature on the desirable fraction of the bio-oil produced from corn cob and corn stalk in the fixed-bed reactor.

undesirable compounds in the bio-oil produced, which are represented in the current study by the main oxygen containing groups present (carboxylic acids, alcohols and carbonyls) the differences in the non-catalytic runs were not that distinguishable. The effect of feedstock in the pyrolysis product yields and composition is difficult to be explained because of the variety and complexity of reactions paths in pyrolytic chemistry involving the formation of free radicals and also the variety of reaction products that may be obtained from the reactions [28]. The differences in the composition of cellulose, hemicellulose, lignin are expected to affect the degradation and pyrolysis paths and rates.

The effect of temperature in the liquid composition and as it is shown in Fig. 11a and b, shows a trend in increase of the desirable components, such as hydrocarbons and phenols for both feeds tocks with an increase in temperature, which can be explained by the enhancement of the degradation of lignocellulosic molecules to lower molecular weight compounds at elevated temperature.

3.4. Catalytic pyrolysis in the fixed-bed reactor

3.4.1. Product yields

In terms of product yields and as it can be seen from the Table 3, the main effect due to the action of the catalyst is the increase in the production of water, which is indicated in Table 3 both by an increase in the water production and a decrease in the organics yield. The water in pyrolysis is produced through a variety of reactions, which are favored from the presence of the catalyst.

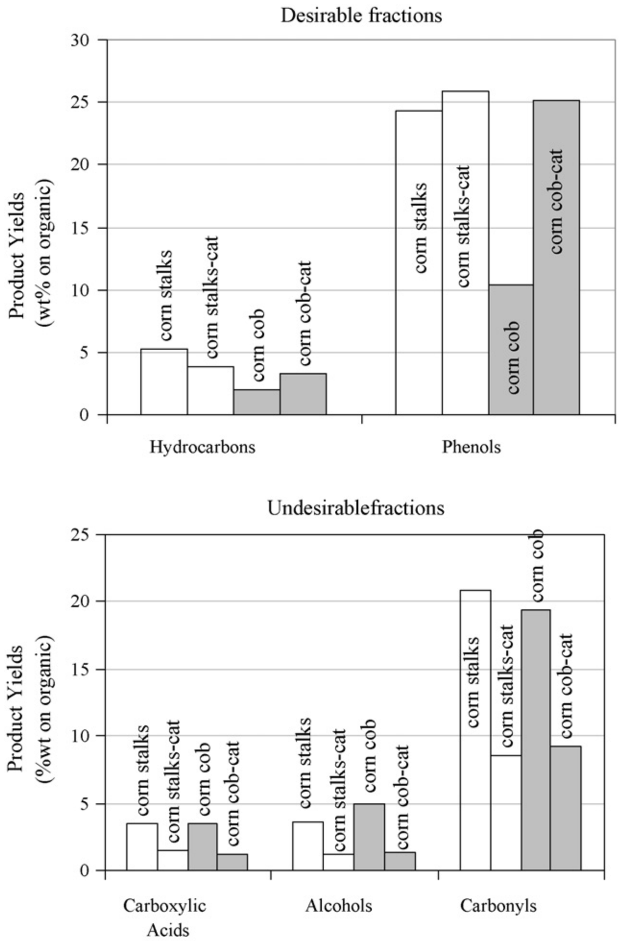


Fig. 12. (a and b) Effect of catalyst in the bio-oil produced from the fixed-bed reactor.

3.4.2. Gas composition

Apart from the hydrogen concentration, we could generally conclude that the presence of catalyst does not significantly alter the individual gas composition. A significant increase due to the catalyst has been recorded in the case of corn cob in terms of hydrogen (almost 4.5 vol% on the gas produced). The levels of the remaining hydrocarbons and CO, CO_2 present in the gas produced were unaffected in the presence of catalyst.

The heating value of the gas products from the catalytic experiments of corn cob is higher than the one from corn stalk. Fig. 10 shows the values at 500 °C.

3.4.3. Liquid products

Aromatic compounds in biomass pyrolysis are considered to be products of the decomposition of polysaccharides, such as lignin. The increase in fractions of aromatic compounds, such as phenols in the presence of the catalytic material is attributed to their enhancement of the cracking and reforming mechanisms and more specifically reactions such as decarboxylation, decarbonylation, dehydration and aromatization reactions. The strongest effect in terms of phenols production in the current study has been observed in the case of corn stalks as indicated in Fig. 12a and can be explained by the higher levels of lignin found in the corn stalks compared to other parts of the crop [29]. As already mentioned, the lignin content is directly related to the phenols production through the pyrolysis mechanism. Also, the presence of catalyst, considering all the other parameters constant, are expected to favor secondary reactions and increase the number of lower molecular weight compounds in the produced bio-oil [5]. In the current study the most significant catalytic effect in the pyrolysis products is the decrease in the fractions of undesirable compounds (acids, alcohols, carbonyls) as indicated in Fig. 12b.

3.5. Comparison of the results obtained in both reactor configurations

Although some differences in the absolute values have been observed, the main trends in both reactors are comparable under similar experimental conditions. In general the gaseous products increase with temperature and the liquid seems to reach a maximum at about 500 °C. The char seems to have different trend in the two reactors. In the captive sample it decreases with temperature for corn cob, whereas for corn stalk it decreases and then increases at high temperatures. In the fixed-bed reactor the trend is to increase up to a maximum for both samples and then decrease. The fluctuations in the char yield were attributed to the production of either gas or liquid product.

In terms of the gaseous composition an increase in the production of CO and H_2 and a decrease in the production of CO_2 have been observed in experiments performed in both reactor configurations, which was attributed to the enhancement of gasification reactions at higher temperatures.

The experiments in the fixed-bed reactor gave higher liquid yields than in the captive sample (fast pyrolysis). The yield of liquids can be increased by increasing the flow rate of the carrier gas. High flow rates of the carrier gas minimizes the vapor residence time in the reaction zone and thus the secondary reaction so this difference might be due to the different flow rates of the carrier gas in the two reactors. In the fixed-bed reactor the flow rate of N_2 was 100 ml/min, where He in the captive sample was 35 ml/min. Higher yields of gas products in the captive sample reactor might also due to the difference in the flow rate. The higher yields of char are explained by differences in temperature, as the higher values were taken by the lower temperatures. Differences are also observed in the gas composition. The gas products from the captive sample reactor gave higher percentage of syngas and lower CO_2 comparing to the gas from fixed-bed reactor, which is an indication that the captive sample is more appropriate for gasification reactions at higher temperatures. The heating value of the gaseous products from both reactors differs mainly at 500 °C for both feed stocks and at 600 °C only for stalks. The difference in the behaviour of both types of corn under study was not always significant. Two interesting findings were that the corn cob produced higher amount of CO in the gaseous fraction and the corn stalks more phenols in the liquid fraction and this is believed to be directly connected to the higher amount of cellulose and hemicellulose to the corn cob compared to the corn stalks.

The main effect of the catalyst was the aqueous phase which was increased decreasing the organic phase. In the gas composition the effect of catalyst was observed only in the increased H_2%, especially in corn cob. In the liquid composition an increase in the fraction of high value chemicals (such as phenols) and a decrease in the heavier undesirable fractions was a promising indication for further catalytic investigations in corn pyrolysis. From the results of the heating value of the gas products at 500 °C, catalyst seems to increase the value slightly.

4. Conclusions

The results of the present experimental study showed that:

- The trends in the main pyrolysis products were comparable in both reactors configurations and the difference in absolute values can be explained based on differences in the reactors configuration and conditions (e.g. flow rates).
- Comparing the two types of corn feedstocks results are comparable but corn cob seems to be easier degraded to lighter products and corn stalk to be a better source of phenols.
- The gas products from the captive sample reactor gave higher percentage of syngas and lower CO_2 comparing to the gas from fixed-bed reactor.
- Considering gas and char heating value from corn residues fast pyrolysis it can be said that corn, generally, is promising material for energy production.
- Concerning the low heating value of the corn stalk pyrolysis gas (13–15 MJ m^3), this is suitable for energy production through gasification at higher temperatures.
- From the other hand, corn cob is suggested for solid biofuels and/or activated carbon production.
- Finally the presence of catalyst seems to increase the quality of both the liquids and the gases produced.
- In the gas composition the effect of catalyst was observed only in the increased H_2%, especially in corn cob.
- In the liquid composition an increase in the fraction of high value chemicals (such as phenols) and a decrease in the heavier undesirable fractions was a promising indication for further catalytic investigations in corn pyrolysis.
- From the results of the heating value of the gas products at 500 °C, catalyst seems to increase the value slightly.
- The results of the experimental study were compared with data reported in the literature and a good agreement observed.

Investigating the potential of corn residues for energy, fuel, materials and chemicals production according to their thermochemical treatment products yields and quality, it can be stated that:

(a) *corn stalks* could be suitable raw material for energy production via gasification at high temperature, due to their medium LHV of pyrolysis gas (13–15 MJ/m^3);
(b) *corn cob* could be a good solid biofuel, due to the high LHV (24–26 MJ/kg) of the produced char;
(c) additionally, corn cobs could be a good material for activated carbon production after being activated or gasified with steam, due to its high fixed carbon content (~74 wt%);
(d) liquid was the major pyrolysis product from *catalytic pyrolysis* (about 40–44 wt% on biomass) for both feedstocks; further analysis of the organic phase of the liquid products were hydrocarbons and phenols, which make them interesting for chemicals production.

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